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PRODUCTS BASED ON PARTICLES OF POLYMER CONTAINING MELANISTIC  
PIGMENTS, ITS PROCESS OF PREPARATION AND ITS USE, PARTICULARLY IN  
COSMETICS

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[Abstract]

A product consisting of particles of polymers, characterized by the fact that the particles of polymers are chosen from the particles of:

- (a) polymers derived from keratin, possibly modified;
- (b) silk fibroin;
- (c) polymers derived from chitin, possibly deacetylated;
- (d) synthetic polymers chosen from:

- (i) crosslinked polymethylmethacrylate;
- (ii) crosslinked poly- $\beta$ -alanine;
- (iii) hollow microspheres of the copolymer of vinylidene chloride and

acrylonitrile;

- (iv) porous microspheres of polyamide 12, polyamide 6 or copolyamide 6/12;
- (v) silicone powders consisting of gums, resins, elastomers of

organopolysiloxanes, these particles having a grain size less than 100 microns and having on the surface and/or in the polymer network a natural or synthetic melanistic pigment, this pigment being either formed beforehand and absorbed by the particles or formed in situ by oxidation of an indole-containing coloring agent.

The present invention relates to new products consisting of fine particles of polymer, containing melanistic pigments, their process of preparation and their use, particularly in the domain of cosmetics, for makeup of body hair and skin, protection of the human epidermis from UV radiation and coloring of hair.

The color of the hair, skin and body hair of human origin comes mainly from melanistic pigments secreted by melanocytes, and furthermore, the protective role of melanistic pigment with regard to solar radiation is well known.

These pigments, of natural origin, include in particular, black or brown pigments called eumelanins.

Their natural biosynthesis occurs in several steps by polymerization of the products of oxidation of an amino acid: tyrosine and one of its oxidation products is 5,6-dihydroxyindole which in turn polymerizes into eumelanin.

Attempts have already been made to manufacture in vitro pigments based on pseudomelanin or compounds similar to melanin which are nontoxic and nonallergenic and which prove in particular to be of value in makeup compositions for the skin, body hair, eyelashes, eyebrows, for which one looks for pigments with suitable safety with respect to the pigments ordinarily used, such as the pigments based on iron oxide.

The applicant discovered, and this is the object of the invention, that it was possible to prepare with good yield a product consisting of fine particles based on particular polymers defined hereafter and a melanistic pigment.

The pigment formed by oxidation of 5,6-dihydroxyindole, possibly associated with 2-carboxy-5,6-dihydroxyindole, is called a melanistic pigment.

By analogy and simplification, the pigment formed by oxidation of each of the compounds with formula (I) defined hereafter will also be called "melanistic pigment."

These new products can be used as pigments or additives in various technical domains in which one uses pigmented particles, such as the domains of paint, cosmetics, ...

The products according to the invention are used more particularly as pigments in the cosmetics industry, particularly for protection of the human epidermis from the harmful effects of solar radiation, for makeup of the skin, body hair, eyelashes and eyebrows and coloring of the hair.

The present invention therefore relates to a product consisting of fine particles of particular polymers, containing melanistic pigments.

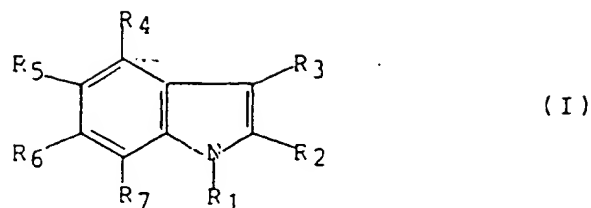
The invention also relates to the preparation of such a product.

The invention also relates to the cosmetic application of such products, particularly in makeup of the skin and body hair (eyelashes and eyebrows), protection of the human epidermis from UV radiation and coloring of the hair.

Other objectives of the invention will appear upon reading of the following description and examples.

The product according to the invention is essentially characterized by the fact that it is made up of particles of polymers defined hereafter having a grain size less than 100 microns and having on the surface and/or in the polymer network, a natural or synthetic melanistic pigment, which is either formed in situ or formed beforehand and absorbed by the polymer particles.

The melanistic pigment results particularly from the oxidation of at least one indole-containing coloring agent, corresponding to the formula:



in which:

$R_1$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl group;

$R_2$  and  $R_3$ , identical or different, represent a hydrogen atom, a  $C_1$ - $C_4$  alkyl group, a carboxyl group or a  $C_1$ - $C_4$  alkoxy carbonyl group;

$R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$ , identical or different, represent a hydrogen atom, a  $C_1$ - $C_4$  alkyl radical, -NHR group (in which R designates H,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl,  $C_2$ - $C_4$  polyhydroxyalkyl), acylamino, carbonyl,  $C_1$ - $C_4$  carboxyalkyl,  $C_1$ - $C_4$  alkoxy carbonyl,  $C_1$ - $C_4$  alkoxy  $C_1$ - $C_4$  carbonylalkyl, carbamyl, halogen,  $C_1$ - $C_4$  mono- or polyhydroxyalkyl,  $C_1$ - $C_4$  aminoalkyl, an OZ group, in which Z designates hydrogen, straight or branched  $C_1$ - $C_{20}$  alkyl, an aralkyl group ( $C_1$ - $C_4$ ), a formyl group, a straight or branched  $C_2$ - $C_{20}$  acyl group, a straight or branched  $C_3$ - $C_{20}$  alkenoyl group,  $-SiR_{11}R_{12}R_{13}$  group,  $-P(O)(OR_8)_2$  group, a  $R_8OSO_2$ - group; with it possible for the radicals  $R_4$  and  $R_5$  or  $R_5$  and  $R_6$  or  $R_6$  and  $R_7$  to form, along with the carbon atoms with which they are connected, a ring possibly containing a carbonyl group, a thiocarbonyl group, a

$\text{>P(O)(OR}_8\text{)}$  group or a  $\text{>CR}_9\text{R}_{10}$  group;

provided that at least one of the radicals  $R_4$ - $R_7$  represents an OZ group or -NHR, or  $R_4$  and  $R_5$  or  $R_5$  and  $R_6$  or  $R_6$  and  $R_7$  form a ring,  $R_8$  and  $R_9$  represent a hydrogen atom or a  $C_1$ - $C_4$  lower alkyl group,  $R_{10}$  represents a  $C_1$ - $C_4$  alkoxy group or a mono- or di( $C_1$ - $C_4$ )alkylamino group,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$ , identical or different, represent straight or branched  $C_1$ - $C_4$  alkyl groups, and the corresponding salts of the alkaline metals, alkaline-earth metals, of ammonium and of amines.

The indole-containing coloring agents are preferably chosen from 4-hydroxyindole, 4-hydroxy-5-methoxyindole, 4-hydroxy-5-ethoxyindole, 5-hydroxyindole, 2-carboxy-5-hydroxyindole, 5-hydroxy-6-methoxyindole, 6-hydroxyindole, 6-hydroxy-7-methoxyindole, 5-methoxy-6-hydroxyindole, 7-hydroxyindole, 5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole,

3-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, (5 or 6)-acetoxy (6 or 5)-hydroxyindole.

The grain size of the particles is generally greater than 0.01 micron and is preferably between 0.01 and 50 microns, and in particular between 0.1 and 20 microns.

They are preferably spherical.

The polymers which can be used according to the invention are polymers which are essentially insoluble in the reaction medium and are chosen from the natural or synthetic polymers, organic or inorganic, with a crosslinked, crystalline or amorphous network, having a molecular weight between 5000 and 5,000,000, which are defined hereafter.

The essentially insoluble character of the polymer is justified by essentially economic reasons inasmuch as the melanistic pigment must be attached on a solid particle support in order to form the product according to the invention.

The solubility of the polymers in the reaction medium must not exceed 10% preferably.

These natural or synthetic polymers are chosen from:

a) the polymers derived from keratin which are in particular chosen from animal or human keratins, which come, for example, from materials chosen from hair, wool, skin, fur, silk, feathers, scales and more particularly hooves, horns.

These materials are preferably washed and/or degreased and then reduced to particles.

Other polymers derived from keratin are chemically modified keratins, with a molecular weight between 10,000 and 250,000, and in particular partially hydrolyzed keratin (or keratin hydrolysate), obtained from skins which are rich in sulfur products and have a molecular weight between 50,000 and 200,000. This hydrolysate is preferably obtained by moderate alkaline hydrolysis.

Products of this type are, for example, sold under the name Kerasol by the company Croda.

Other modified keratins are the sulfonic keratins with a molecular weight between 10,000 and 100,000 obtained from goose or chicken feathers or even more advantageously from hooves or horns.

This keratin is obtained by oxidation of all or part of the disulfide bonds of the cystine groups of the keratin into cysteic acid groups:  $\text{SO}_3\text{H}$ , with the oxidation advantageously performed in an acid medium, such as formic acid, by means of an oxidizing agent such as hydrogen peroxide.

b) Silk fibroin.

c) The polymers derived from chitin: they are made up of chitin which is a natural polymer, the largest source of which is in the shells of crustaceans, such as crabs, lobsters, crayfish, etc... The chitin is prepared according to a process described in particular in the work of

R.A.A. Muzzarelli, "Chitin," published at Pergamon Press Oxford, 1977, pp. 89-100 and 207-217. It is also possible to use its deacetylated derivative known by the name chitosan, which is obtained by saponification of the acetyl groups of the chitin.

Chitosan, as offered commercially, is particularly acetylated and contains 70-90 wt% chitosan. It is also possible to use it in the form of one of its insoluble salts, such as the sulfates and phosphates. Products of this type are sold, for example, under the name Kytex by the company Hercules.

d) The synthetic polymers are chosen from:

(i) crosslinked polymethylmethacrylate, such as the product sold under the name MicroPearl M 305 by the company Seppic;

(ii) crosslinked poly- $\beta$ -alanine, as described in the French patent 2,530,250, or else advantageously presented in the form of microspheres with a very low size spread, 85 wt% having a grain size between 28 and 46 microns. These poly- $\beta$ -alanines are obtained according to a process consisting of polymerizing, at between 60 and 100°C, and preferably at around 80°C, acrylamide in a mixture of t-butanol/toluene solvents, in ratios between 1:24 and 10:1 and preferably between 1:6 and 6:1, in the presence of a polymerization initiator, an octadecene-maleic anhydride copolymer as a suspension agent, and then subjecting the obtained suspension of poly- $\beta$ -alanine to crosslinking using a dialdehyde, such as glutaraldehyde.

The polymerization initiator is preferably sodium or potassium tertibutylate (0.1 to approximately 2 mol% with respect to the acrylamide).

The glutaraldehyde is used in the form of an aqueous solution [containing] between 20 and 25%, and in a proportion between 1 and 15 wt% and preferably between 1 and 8 wt% with respect to the starting acrylamide weight;

(iii) hollow microspheres of a copolymer of vinylidene chloride and acrylonitrile, sold under the name Expancel by the company Kema Nord;

(iv) porous microspheres of polyamide 12, polyamide 6 or copolyamide 6/12, sold under the name Orgasol by the company Ato-Chimie. These microspheres preferably have a grain size between 10 and 15 microns;

(v) silicone powders which are gums, resins and more particularly elastomers of organopolysiloxanes.

The products according to the invention are prepared according to a process consisting essentially of mixing, in the air and at preferably room temperature and which can range up to 100°C, the indole compound with formula (I) and the particles of the polymers described above, in a medium which is essentially a nonsolvent of the polymer, as defined above.

If one uses no oxidizing agents other than oxygen in the air, one operates preferably at an alkaline pH, in which case the pigment forms gradually and becomes attached on the particles



and/or in the network or the pores of these particles. It is also possible to use a metallic oxidation catalyst, such as the cupric ion in the presence of oxygen.

These products can also be prepared by proceeding with an immediate formation of the melanistic pigment, using an oxidizing agent such as hydrogen peroxide, periodic acid and its hydrosoluble salts and derivatives, the permanganates and bichromates, such as those of sodium or potassium, sodium hypochlorite, potassium ferricyanide, ammonium persulfate, silver oxide, ferric chloride, lead oxide (Pb IV), sodium nitrite, by addition of iodide and hydrogen peroxide, the iodide being preferably an iodide of an alkaline metal, of an alkaline-earth metal or of ammonium.

These oxidizing agents can be activated possibly by a pH modifying agent.

For the products intended for cosmetic application, one preferably uses as oxidizing agents, hydrogen peroxide, periodic acid and its salts, potassium permanganate, sodium hypochlorite, ammonium persulfate, sodium nitrite and the iodide/hydrogen peroxide system.

The order of addition of the compounds involved in the preparation of the product, according to the invention, is of little importance provided that the oxidizing agent is incorporated last when it is used without a pH modifying agent, and in the case of the iodide/hydrogen peroxide system, either the hydrogen peroxide or the iodide is introduced last.

In the case in which a pH modifying agent is used to activate the oxidizing agent, it is preferable to add either the oxidizing agent or the pH modifying agent last.

When a keratin hydrolysate is used, the pH of the medium must preferably be less than 5 in order to avoid solubilization of the modified keratin.

When a sulfonic keratin is used, the medium is either essentially alcoholic or aqueous, in which case the pH must be less than 7.

When chitosan is used, the aqueous medium must preferably have a pH greater than 5.8.

As indicated above, the reaction medium is a medium which is essentially a nonsolvent of the polymer in consideration. It preferably consists of water, and it can possibly consist of a mixture of water and solvent, the solvent being chosen from ethyl alcohol, isopropyl alcohol, tertio-butyl alcohol, the monomethyl, monoethyl, monobutyl ethers of ethylene glycol, the acetate of the monoethylether of ethylene glycol.

These solvents must furthermore be able to solubilize the indole coloring agent.

When the medium consists of a water-solvent(s) mixture, the solvents are present in concentrations preferably between 0.5 and 90 wt% with respect to the total weight of the composition, and in particular between 2 and 50 wt%, and preferably between 2 and 20 wt%.

Their nature is chosen and their proportion adjusted as a function of the criteria of solubility of the indole derivatives and the criterium of insolubility of the polymer.

In the process according to the invention, one preferably uses the indole coloring agent in weight proportions between 0.1 and 10% and preferably between 1 and 5 wt%, the polymer representing 0.05-50 wt% and preferably 4-30 wt%, the rest of the reaction mixture generally consisting of water or a water/solvent mixture.

The oxidizing agents are used in sufficient quantities to oxidize the indole coloring agent and to form the melanistic pigment.

When the iodide ion is used to form the melanistic pigment, it is preferably used in proportions of 0.07-4% and in particular between 0.7 and 3%, while observing an indole coloring agent/I<sup>-</sup> ratio between 0.6 and 6.

The proportions are determined with respect to the weight of the reaction medium.

For the preparation of the particles of polymer containing a melanistic pigment, it is possible to use a natural or synthetic melanistic pigment prepared beforehand which is attached to the surface of the particles or is absorbed by them. In this case, the finely divided melanistic pigment is dispersed in a medium which is a nonsolvent of the polymer. After absorption of the pigment, the particles are dried.

The product in the form of particles is preferably used in the cosmetic domain in which it is preferably present in spherical form. It can be added to conventional cosmetic supports at a concentration between 0.2 and 35 wt% and preferably between 2 and 20 wt% with respect to the total weight of the composition, resulting in cosmetic compositions protecting the human epidermis, makeup products, particularly for the eyelashes, eyebrows or skin, such as eye shadows, rouges, liners also called "eyeliners," mascaras for the eyelashes and eyebrows, or else dye compositions for the hair. These cosmetic supports are known in themselves.

These compositions can be present in the form of a lotion, a thickened lotion, a gel, a cream, a milk, a powder, a stick and can possibly be packaged in aerosol form and be present in the form of a foam.

When the compositions are used for skin, eyelash and eyebrow makeup, they can in particular be present in solid or paste, anhydrous or aqueous form, as opposed to oil-in-water or water-in-oil emulsions or suspensions. These compositions have the advantage of being stable and of being suitably harmless.

When the compositions are used for the protection of the human epidermis from UV radiation, they consequently constitute so-called "sun" compositions; they can be present in the form of suspensions or dispersions in solvents or greasy substances, in the form of emulsions such as creams or milks, gels, solid sticks or aerosol foams.

In all cases, when they are used in the form of emulsions, they can moreover contain surfactants well known in the state of the art, chosen from the anionic, nonionic, cationic or amphoteric surfactants.

The makeup compositions and the sun compositions can also contain greasy substances, organic solvents, silicones, thickeners, softeners, solar filters, antifoaming agents, hydrating agents, perfumes, preservatives, antioxidants, charges, sequestering agents, processing agents such as anionic, cationic, nonionic, amphoteric polymers, as well as mixtures of them, propellants, alkalizing agents or acidifying agents.

The greasy substances can consist of an oil or a wax or a mixture of them, fatty acids, fatty alcohols, paraffin, lanolin, hydrogenated lanolin, acetylated lanolin.

The oils are chosen from the animal, plant, mineral or synthetic oils and particularly hydrogenated palm oil, hydrogenated castor oil, petrolatum oil, paraffin oil, Purcellin oil.

The waxes are chosen from the animal, fossil, plant, mineral or synthetic waxes, among which can be mentioned bees wax, carnauba wax, candelilla wax, sugarcane, Japan waxes, lignite waxes, montan wax, microcrystalline waxes, paraffins.

In addition to the ultrafine particles containing melanistic pigments, as defined above, the compositions can also contain other pigments generally used in cosmetics, particularly the pearlescent pigments allowing one to further vary the colorings which can be obtained.

The following examples are intended to illustrate the invention without having any limiting character.

#### Example 1

One prepares a powder of polymer and melanistic pigment by successively adding the following ingredients in a beaker with magnetic stirring:

- 3% Crosslinked poly- $\beta$ -alanine (approximately 2 microns)	4.9 g
- 5,6-Dihydroxyindole	1.0 g
- Water	91.4 g
- Sodium nitrite	2.7 g
- HCl (1N) qs pH = 4	

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

#### Example 2

One prepares a powder of polymer and melanistic pigment by successively adding the following ingredients in a beaker with magnetic stirring:

- 6-Hydroxyindole	1.7 g
- Ethyl alcohol	13.2 g
- Water	69.5 g
- Ammonium iodide	1.1 g
- Crosslinked poly- $\beta$ -alanine (grain size between 0.1 and 1 micron)	9.9 g
- H <sub>2</sub> O <sub>2</sub> (aqueous solution containing 20 volumes)	4.6 g

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine red ochre powder.

### Example 3

One prepares a chitomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	1.5 g
- Ethyl alcohol	12.4 g
- Water	73.1 g
- Potassium iodide	0.7 g
- Chitin extracted from crustacean shells, sold under the name Chitin LS 2970 by the company Laboratoire Serobiologique de Nancy	1.6 g
- Aqueous solution of hydrogen peroxide containing 30 volumes	10.7 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

### Example 4

One prepares a chitomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	1.1 g
- Water	96.0 g
- Chitin extracted from crustacean shells, sold by the company Laboratoire Serobiologique de Nancy under the name Chitin LS 2970	1.9 g
- Sodium periodate	1.0 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

#### Example 5

One prepares a chitomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 6-Hydroxyindole	2.8 g
- Ethyl alcohol	24.9 g
- Water	69.2 g
- Chitin extracted from crustacean shells, sold by the company Laboratoire Serobiologique de Nancy under the name Chitin LS 2970	1.4 g
- Ammonium persulfate	1.7 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine powder with a purplish-red coloring.

#### Example 6

One prepares a chitomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 5-Methoxy-6-hydroxyindole	0.8 g
- Ethyl alcohol	31.7 g
- Water	63.4 g
- Chitin extracted from crustacean shells, sold by the company Laboratoire Serobiologique de Nancy under the name Chitin LS 2970	0.9 g
- Potassium permanganate in 1N aqueous solution: 3.2 g	0.51g MA

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine ashy mauve-violet powder.

#### Example 7

One prepares a chitomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 2,3-Dimethyl-5,6-dihydroxyindole hydrobromide	3.0 g
- Ethyl alcohol	27.6 g
- Water	66.3 g
- Chitin extracted from crustacean shells, sold by the company [Laboratoire] Serobiologique de Nancy under the name Chitin LS 2970	1.7 g
- Sodium nitrite	1.4 g

The ultrafine powder, after filtration, washing with water and then with ethyl alcohol, has a mauve coloring.

#### Example 8

One prepares a chitomelanistic compound by mixing the following compounds with magnetic stirring:

- Chitosan sold under the name Kytex M by the company Hercules	10.7 g
- Water alkalized by NaOH	
Water	75.9 g
NaOH	1.4 g
- 5,6-dihydroxyindole	1.7 g
- Ethyl alcohol	10.3 g

To the chitosan powder in suspension in the alkaline water, the 5,6-dihydroxyindole in solution in ethyl alcohol is added. The black precipitate obtained is separated by filtration, washing with water and then with ethyl alcohol.

#### Example 9

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (brown hair washed and reduced to a powder)	2.1 g
- 5,6-Dihydroxyindole	0.8 g
- Ethyl alcohol	21.1 g
- Water	76.0 g

One allows the reaction to finish in air (15 min) before filtering the ultrafine beige-gray powder which is obtained.

Example 10

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	1.0 g
- Ethyl alcohol	24.4 g
- Water	57.0 g
- Keratin (brown hair washed and reduced to a powder)	1.3 g
- NaOH in 1N aqueous solution (16.3 g)	0.65 g MA

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine medium-gray powder.

Example 11

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (white hair washed and reduced to a powder)	0.8 g
- 7-Hydroxyindole	1.0 g
- Potassium iodide	1.0 g
- Ethyl alcohol	14.0 g
- Water	69.2 g
- H <sub>2</sub> O <sub>2</sub> (aqueous solution containing 30 volumes)	14.0 g

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine very dark brown powder.

Example 12

One prepares a keratino-melanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (gray hair washed and reduced to a powder)	1.9 g
- 4-Hydroxyindole	1.2 g
- Ethyl alcohol	23.1 g
- Water	70.1 g
- Sodium periodate	3.7 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine bluish-black powder.

### Example 13

One prepares a keratino-melanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (from brown hair washed and reduced to a powder)	1.4 g
- 5-Methoxy-6-hydroxyindole	2.8 g
- Ethyl alcohol	41.7 g
- Water	51.4 g
- Potassium permanganate (1N aqueous solution: 2.7 g)	0.43 g MA

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

### Example 14

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (brown hair washed and reduced to a powder)	1.1 g
- 6-Hydroxyindole	1.1 g
- Ethyl alcohol	22.0 g
- Water	74.7 g
- Ammonium persulfate	1.1 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

### Example 15

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:



- Keratin (gray hair washed and reduced to a powder)	1.0 g
- 3-Methyl-5,6-dihydroxyindole	1.0 g
- Ethyl alcohol	9.8 g
- Water	87.6 g
- Sodium nitrite	0.6 g
- HCl (1N) qs pH = 4.9	

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine brown powder.

#### Example 16

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (gray hair washed and reduced to a powder)	3.2 g
- 4-Hydroxyindole	3.2 g
- Ethyl alcohol	32.0 g
- Water	60.8 g
- Sodium periodate	0.8 g

The periodate [sic; pigment] forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine bluish medium-gray powder.

#### Example 17

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Keratin (gray hair washed [and] reduced to a powder)	1.0 g
- 5-Hydroxyindole	1.7 g
- Ethyl alcohol	9.8 g
- Water	86.5 g
- Ammonium persulfate	1.0 g

The pigment forms as soon as the oxidizing agent is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine olive-brown powder.

#### Example 18

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Sulfonic keratin (from bovine hooves)	4.3 g
- 5,6-Dihydroxyindole	0.9 g
- Sodium iodide	0.9 g
- Ethyl alcohol	87.0 g
- H <sub>2</sub> O <sub>2</sub> (aqueous solution containing 30 volumes)	2.2 g

The pigment forms as soon as the hydrogen peroxide is added.

After filtration, washing with water and then with ethyl alcohol, one obtains an ultrafine black powder.

#### Example 19

One prepares a keratinomelanistic compound by successively adding the following ingredients in a beaker with magnetic stirring:

- Sulfonic keratin (from bovine hooves)	6.1 g
- 6-Hydroxyindole	1.8 g
- Ammonium iodide	0.4 g
- Ethyl alcohol	81.9 g
- H <sub>2</sub> O <sub>2</sub> (aqueous solution containing 30 volumes)	9.8 g

The pigment forms as soon as the hydrogen peroxide is added.

After filtration and washing with ethyl alcohol, one obtains an ultrafine dark brown powder.

#### Example 20

(I) Preparation of crosslinked poly- $\beta$ -alanine.

Into a 3-L reactor, provided with an "anchor"-type stirrer with a diameter of 90 mm, a nitrogen intake, an addition funnel, and a distillation column head, one introduces: 934 g toluene, 1666 g tertibutanol and 1.4 g maleic anhydride/octadecene copolymer (sold under the name

PA-18) by the company Gulf. After heating of this mixture to 70°C, 100 g acrylamide are added to it. The temperature is then brought to 100°C, and 120 mL of the water/toluene/tertobutanol mixture are distilled. After the end of distillation, the reaction mixture is cooled to 80°C, and the speed of stirring is adjusted to 550 rpm. A solution of 2.24 g potassium tertobutylate in 40 g tertobutanol is then added over 10 min. The addition bulb is rinsed with 120 mL toluene. After 7 h of stirring at 80°C, one allows it to return to room temperature. 7.5 mL 12N hydrochloric acid are then added drop by drop to the mixture.

To the suspension of microspheres obtained, one adds, with intense stirring (550 rpm), at 50°C, 100 mL water over 15 min, and then 15 mL of a 25% glutaraldehyde solution over 20 min. After the stirring is maintained for 4 h at this temperature, it is allowed to return to room temperature. After settling, the supernatant solvents are eliminated, and the microspheres are washed twice with 500 mL ethanol. Spin drying after each washing is done by centrifugation (3500 rpm). Washing with 15 liters water is then done continuously; then, the water is eliminated until a final volume of the mixture of 600 mL is obtained.

The crosslinked poly- $\beta$ -alanine is then dried by lyophilization, and one obtains 92 g of white powder of which the diameter of the microspheres is on the average  $0.37 \pm 0.2$  microns.

The percentage of crosslinking, that is to say the glutaraldehyde/acrylamide ratio, is approximately 3%.

## (II) Preparation of particles containing the melanistic pigment

### Mode of operation (IIa)

0.55 g 5,6-dihydroxyindole is dissolved in 40 g water; it is then adjusted to pH 9 by a solution of NaOH (1N). 10 g of the microspheres prepared according to (I), soaked by a few drops of ethanol, are introduced into it. It is heated to 40°C and then stirred with the rotovapor for 40 min. A colorless dispersion is obtained. 1.25 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in solution in 10 g of water are introduced into it. In the brown-colored suspension, oxygen is bubbled for 2 h. The blackened microspheres are left with stirring for a night at room temperature in an oxygen atmosphere and then washed until the washing water is colorless and neutral; the particles are dried by lyophilization.

### Mode of operation (IIb)

a) 40 g microspheres prepared according to (I) are swollen by a solution composed of 10 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 400 g water. The mixture is stirred for 1 h at room temperature and then lyophilized.

b) 0.2 g 5,6-dihydroxyindole is dissolved in 80 g water; then it is adjusted to pH 9 by a solution of NaOH (1N). In this solution, 20 g microspheres prepared above (a) are dispersed. The oxidation of the blackened suspension is completed according to the mode of operation (IIa).

#### Example 21

One prepares a powder of polymer and melanistic pigment by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	5.0 g
- Ethyl alcohol	6.6 g
- Crosslinked polymethylmethacrylate, sold under the name	3.7 g
Micro-Pearl M 305 by the company Seppic	3.7 g
- Ammonium persulfate	1.5 g
- Water	qsp 100.0 g

After filtration, washing with water and then with alcohol, one obtains an ultrafine very dark-gray powder.

#### Example 22

One prepares a powder of polymer and melanistic pigment by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	11.1 g
- Ethyl alcohol	16.7 g
- Water	55.5 g
- Polyamide 12 sold under the name Orgasol 2002 D Naturel	
by the company Ato-Chimie	11.1 g
- Pure NaOH	5.6 g

One allows the reaction to finish in the air (4 h) before filtering the ultrafine black powder which is obtained, which is separated by filtration, washing with water and then with alcohol.

#### Example 23

One prepares a powder of polymer and melanistic pigment by successively adding the following ingredients in a beaker with magnetic stirring:

- 5,6-Dihydroxyindole	11.1 g
- Ethyl alcohol	16.7 g
- Water	55.5 g
- Vinylidene chloride/acrylonitrile copolymer in microsphere form, sold under the name Expancel 551 WU by the company Kema Nord	11.1 g
- Pure NaOH	5.6 g

One allows the reaction to finish in air (1 h) before filtering the ultrafine very dark-gray powder which is obtained, which is separated by filtration, washing with water and then with alcohol.

#### Example 24

A coloring composition for treatment of gray hair is prepared by proceeding to mix the following ingredients:

- Product prepared according to Example 20 (IIa or IIb)	1.0 g
- Crosslinked polyacrylic acid, sold under the name Carbopol 940 by the company Goodrich	0.7 g
- N-vinylpyrrolidone-vinyl acetate copolymer, sold by the company GAF under the name PVP/VA-S-630	2.0 g
- Ethanol	17.0 g
- Emulsion based on cationic silicone, sold by Dow Corning under the name DC 929	0.1 g
- Triethanolamine qsp pH = 6.6	
- Water	qsp 100.0 g

5 g of this composition are applied on a tuft of gray hair. After drying, the hair is colored in a medium-gray shade.

#### Example 25

One prepares a mascara with the following composition:

- Triethanolamine stearate	15.0 g
- Candelilla wax	8.0 g
- Carnauba wax	10.0 g
- Hydroxyethylcellulose	1.0 g

- Gum arabic	1.0 g
- Product according to Example 18	8.0 g
- Methyl parahydroxybenzoate	0.15 g
- Propyl parahydroxybenzoate	0.15 g
- Exchanged water	qsp 100.0 g

In this example, it is possible to replace the product of Example 18 by that of Example 19.

#### Example 26

An eyeliner with the following composition is prepared:

- Propylene glycol	8.0 g
- Polyethylene glycol	5.0 g
- Isopropanolamine myristate	3.0 g
- Xanthan gum	1.0g
- Polyvinyl alcohol	0.5 g
- Hydrogenated lanolin	4.0 g
- Methyl parahydroxy benzoate	0.1 g
- Propyl parahydroxy benzoate	0.1 g
- Ethyl parahydroxy benzoate	0.1 g
- Titanium mica	5.0 g
- Black pigment (product according to Example 12)	7.0 g
- Exchanged water	qsp 100.0 g

In this example, the product of Example 12 can be replaced by those of Examples 1, 3, 4, 6, 8, 11, 13, 14, 15, 18, 19.

#### Example 27

A foundation with the following composition is prepared:

- Stearic acid	2.2 g
- Glycerol stearate	3.2 g
- Petrolatum oil	4.0 g
- Isopropyl palmitate	9.0 g
- Ethyl-2-hexyl palmitate	8.0 g

- Propyl parahydroxybenzoate		0.1 g
- Triethanolamine		1.1 g
- Glycerol		3.0 g
- Propylene glycol		2.0 g
- Magnesium aluminosilicate		1.0 g
- Sodium carboxymethylcellulose		0.2 g
- Imidazolidinyl urea		0.3 g
- Yellow iron oxide		2.0 g
- Red iron oxide		1.4 g
- Product according to Example 14		0.5 g
- Titanium dioxide		8.0 g
- Talc		5.0 g
- Perfume		0.3 g
- Exchanged water	qsp	100.0 g

In this example, the product of Example 14 can be replaced by those of Examples 2, 5, 9, 10, 11, 13, 14, 15, 20 or 21.

#### Example 28

A sun composition which follows is prepared:

- 2-Octyl-1-dodecanol		10.0 g
- Magnesium stearate		4.0 g
- Beeswax		5.0 g
- Hydrogenated lanolin		1.0 g
- Lanolin		4.0 g
- Sorbitan sesquioleate sold under the name Arlacel 83 by the company ICI		4.5 g
- Mixture of glycerol monodistearate and potassium stearate (9317)		1.0 g
- Petrolatum oil		27.0 g
- Product prepared according to Example 20 (IIa) or 20 (IIb)		5.0 g
- Preservatives qs		
- Perfume qs		
- Water	qsp	100.0 g

Example 29

In a beaker with stirring, one dissolves 1.34 g 6-aminoindole in a solution consisting of 140 mL water and 18 mL alcohol.

The pH is adjusted to 6.3 by dilute acetic acid. One then adds 9 mL hydrogen peroxide containing 20 volumes and then, in a nitrogen atmosphere, 48.4 g crosslinked poly- $\alpha$ -alanine (prepared according to Example 20).

The crosslinked poly- $\alpha$ -alanine is allowed to swell for 2 h, and a solution of potassium iodide (0.75 g iodide in 7.5 cc water) is added dropwise.

The stirring is maintained for another 2 h, and one filters and washes with water.

One obtains 57.2 g of a black powder.

Example 30

The following composition is prepared:

- Silk fibroin powder		10.0 g
- 5,6-Dihydroxyindole		1.0 g
- Ethyl alcohol		20.0 g
- H <sub>2</sub> O <sub>2</sub> (20 volumes)		20.0 g
- Triethanolamine qsp pH = 8		
- Water	qsp	100.0 g

The ingredients are added one after another with stirring. The coloring of the silk fibroin begins when the pH is brought to 8 by the triethanolamine. The mixture is left with stirring for 1 h.

The solution is then filtered using fritted glass No. 4 (the filtrate is clear). The part collected on the filtered [sic] glass is rinsed successively with water and with alcohol. The obtained powder is dried. Its color is old-fashioned pink (gray pink).

Example 31

The following composition is prepared:

Polydimethylsiloxane in powder form, sold under the name Silicone Powder X2-1605 by the company Dow Corning	10.0 g
- 4-Hydroxyindole	1.0 g
- Ethyl alcohol	10.0 g
- H <sub>2</sub> O <sub>2</sub> (30 volumes)	10.0 g



- 22°Bé [Baumé scale] Ammonia		10.0 g
- Water	qsp	100.0 g

The pH of the solution is 10.6.

The ingredients are added one after the other, except the monohydroxyindole, which is dispersed beforehand in the alcohol.

The oxidative polymerization of the indole begins as soon as the ammonia is added.

The mixture is left with stirring for 10 min; then, the solution is filtered using fritted glass No. 4.

The powder of the fritted [glass] is washed successively with water and with alcohol until the washing liquor is colorless. The color of the dried powder which is obtained is slightly bluish dark gray.

### Claims

1. A product consisting of particles of polymers, characterized by the fact that the particles of polymers are chosen from the particles of:

- (a) polymers derived from keratin possibly modified;
- (b) silk fibroin;
- (c) polymers derived from chitin possibly deacetylated;
- (d) synthetic polymers chosen from:

(i) crosslinked polymethylmethacrylate;

(ii) crosslinked poly- $\alpha$ -alanine;

(iii) hollow microspheres of the copolymer of vinylidene chloride and acrylonitrile;

(iv) porous microspheres of polyamide 12, polyamide 6 or copolyamide 6/12;

(v) silicone powders consisting of gums, resins, elastomers of organopolysiloxanes,

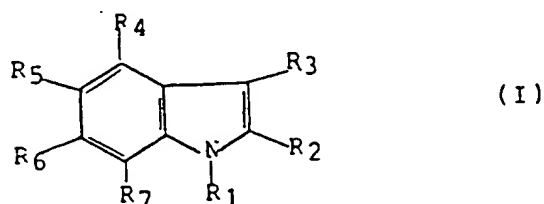
these particles having a grain size less than 100 microns and having on the surface and/or in the polymer network, a natural or synthetic melanistic pigment, this pigment being either formed beforehand and absorbed by the particles or formed in situ by oxidation of an indole-containing coloring agent.

2. A product consisting of particles of polymers, characterized by the fact that the particles of polymers are chosen from the particles of:

- (a) polymers derived from keratin, possibly modified;
- (b) silk fibroin;
- (c) polymers derived from chitin, possibly deacetylated;

(d) synthetic polymers chosen from:

- (i) crosslinked polymethylmethacrylate;
  - (ii) crosslinked poly- $\alpha$ -alanine;
  - (iii) hollow microspheres of the copolymer of vinylidene chloride and acrylonitrile;
  - (iv) porous microspheres of polyamide 12, polyamide 6 or copolyamide 6/12;
  - (v) silicone powders consisting of gums, resins, elastomers of organopolysiloxanes,
- these particles having a grain size less than 100 microns and having on the surface and/or in the polymer network, a melanistic pigment resulting from the oxidation of at least one indole coloring agent corresponding to the formula:



in which:

$R_1$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl group;

$R_2$  and  $R_3$ , identical or different, represent a hydrogen atom, a  $C_1$ - $C_4$  alkyl group, a carboxyl group or a  $C_1$ - $C_4$  alkoxy carbonyl group;

$R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$ , identical or different, represent a hydrogen atom, a  $C_1$ - $C_4$  alkyl radical, -NHR group (in which R designates H,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl,  $C_2$ - $C_4$  polyhydroxyalkyl), acylamino, carbonyl,  $C_1$ - $C_4$  carboxyalkyl,  $C_1$ - $C_4$  alkoxy carbonyl,  $C_1$ - $C_4$  alkoxy carbonyl  $C_1$ - $C_4$  alkyl, carbamyl, halogen,  $C_1$ - $C_4$  mono-or polyhydroxyalkyl,  $C_1$ - $C_4$  aminoalkyl, an OZ group in which Z designates hydrogen, straight or branched  $C_1$ - $C_{20}$  alkyl, an aralkyl group ( $C_1$ - $C_4$ ), a formyl group, a straight or branched  $C_2$ - $C_{20}$  acyl group, a straight or branched  $C_3$ - $C_{20}$  alkenoyl group, a straight or branched  $C_3$ - $C_{20}$  alkenoyl group,  $-\text{SiR}_{11}\text{R}_{12}\text{R}_{13}$  group,  $-\text{P}(\text{O})(\text{OR}_8)_2$  group,  $\text{R}_8\text{OSO}_2$ - group; with it possible for the radicals  $R_4$  and  $R_5$  or else  $R_5$  and  $R_6$  or else  $R_6$  and  $R_7$  to form, along with the carbon atoms with which they are connected, a ring possibly containing a carbonyl group, a thiocarbonyl group, a

$\text{>P(O)(OR}_8\text{)}$  group or a  $\text{>CR}_9\text{R}_{10}$  group;

provided that at least one of the radicals  $R_4$  to  $R_7$  represents an OZ group, or -NHR, or  $R_4$  and  $R_5$  or  $R_5$  and  $R_6$  or  $R_6$  and  $R_7$  form a ring,  $R_8$  and  $R_9$  represent a hydrogen atom or a  $C_1$ - $C_4$  lower alkyl group,  $R_{10}$  represents a  $C_1$ - $C_4$  alkoxy group or a mono- or di( $C_1$ - $C_4$ )alkyl amino group,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$ , identical or different, represent straight or branched  $C_1$ - $C_4$  alkyl groups, and the corresponding salts of the alkaline metals, alkaline-earth metals, of ammonium and of amines.

3. A product according to Claim 1 or 2, characterized by the fact that the grain size of the particles is greater than 0.01 micron, and it is preferably between 0.01 and 50 microns.

4. A product according to Claim 2, characterized by the fact that the indole coloring agent is chosen from 4-hydroxyindole, 4-hydroxy-5-methoxyindole, 4-hydroxy-5-ethoxyindole, 5-hydroxyindole, 2-carboxy-5-hydroxyindole, 5-hydroxy-6-methoxyindole, 6-hydroxyindole, 6-hydroxy-7-methoxyindole, 5-methoxy-6-hydroxyindole, 7-hydroxyindole, 5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, (5 or 6)-acetoxyl (6 or 5)-hydroxyindole.

5. A product according to any one of Claims 1-4, characterized by the fact that said polymers are chosen from the polymers which are essentially insoluble in the reaction medium, in which the oxidation reaction takes place, and that they have a crosslinked, crystalline or amorphous network, and have a molecular weight between 5000 and 5,000,000.

6. A product according to any one of Claims 1-5, characterized by the fact that the keratins are chosen from animal or human keratins, which come from materials chosen from hair, wool, skin, fur, silk, feathers, scales, hooves, horns.

7. A product according to any one of Claims 1-5, characterized by the fact that the polymer derived from keratin is a keratin which is chemically modified, with a molecular weight between 10,000 and 250,000, by hydrolysis or oxidation.

8. A product according to Claim 7, characterized by the fact that the polymer derived from keratin is a partially hydrolyzed keratin, obtained from skin and having a molecular weight between 50,000 and 200,000.

9. A product according to Claim 7, characterized by the fact that the modified keratin is a sulfonic keratin, with a molecular weight between 10,000 and 100,000, obtained from goose or chicken feathers or from hooves or horns.

10. A product according to any one of Claims 1-5, characterized by the fact that the polymers derived from chitin consist of chitin or its deacetylated derivative called chitosan.

11. A product according to any one of Claims 1-5, characterized by the fact that the polymer is a crosslinked poly- $\alpha$ -alanine.

12. A product according to any one of Claims 1-5, characterized by the fact that the polymer is made up of hollow microspheres of vinylidene chloride and acrylonitrile copolymers or porous microspheres of polyamide 12, polyamide 6 or copolyamide 6/12.

13. A process for preparation of a product as defined in any one of Claims 2-12, characterized by the fact that in an aqueous medium, one mixes an indole coloring agent as defined in Claim 2 and a polymer particle load, having a grain size less than 100 microns, and that one then proceeds with the formation of the pigment by oxidation of the indole coloring agent.

14. A process according to Claim 13, characterized by the fact that the oxidation is brought about slowly in air, at alkaline pH.

15. A process according to Claim 13, characterized by the fact that the oxidation is brought about by oxygen in the presence of a metallic catalyst.

16. A process according to Claim 13, characterized by the fact that the oxidation is brought about by addition of oxidizing agents consisting of hydrogen peroxide, periodic acid and its salts, the permanganates, the bichromates, sodium hypochlorite, potassium ferricyanide, ammonium persulfate, silver oxide, ferric chloride, lead oxide (Pb IV), sodium nitrite.

17. A process according to Claim 13, characterized by the fact that the oxidation is brought about by addition of an alkaline, alkaline-earth or ammonium iodide and hydrogen peroxide.

18. A process according to Claim 13, characterized by the fact that the oxidizing agents are chosen from hydrogen peroxide, periodic acid and its salts, potassium permanganate, sodium hypochlorite, ammonium persulfate, sodium nitrite and the iodide/hydrogen peroxide system.

19. A process according to any one of Claims 13-18, characterized by the fact that the reaction medium is a medium which is essentially a nonsolvent of the polymer in consideration, consisting of water or a mixture of water and solvent(s).

20. A process according to Claim 19, characterized by the fact that the solvent is chosen from ethyl alcohol, isopropyl alcohol, tertibutyl alcohol, the monomethyl, monoethyl, monobutyl ethers of ethylene glycol, the acetate of the monoethylether of ethylene glycol.

21. A process according to any one of Claims 13-20, characterized by the fact that the indole coloring agent is present in weight proportions between 0.1 and 10 wt% and preferably between 1 and 5 wt%, with respect to the weight of the reaction medium, the polymer representing 0.05-50 wt% and preferably 4-30 wt% with respect to the weight of the reaction medium.

22. A process for preparation of a product according to Claim 1, characterized by the fact that the melanistic pigment formed beforehand, in the finely divided state, is dispersed in a medium which is a nonsolvent of the polymer and containing said particles of polymer, and that after absorption of the pigment, the particles are dried.

23. A cosmetic composition, characterized by the fact that it contains, in a cosmetically acceptable medium, at least one product as defined in any one of Claims 1-12 or prepared according to the process defined in any one of Claims 13-22.

24. A composition according to Claim 23, characterized by the fact that it is present in the form of a lotion, a thickened lotion, a gel, a cream, a milk, a powder, a stick and that it is possibly packaged in aerosol form.

25. A composition according to Claim 23, which is intended to be used for makeup of the skin, eyelashes and eyebrows, characterized by the fact that it is present in solid or paste, anhydrous or aqueous form.

26. A composition according to either of Claims 23 and 25, which is intended for protection of the human epidermis from solar radiation, characterized by the fact that it is present in the form of suspensions or dispersions in solvents or oily substances or in emulsion, ointment, gel, solid stick or aerosol foam form.

27. A composition according to Claim 23, characterized by the fact that it contains oily substances, organic solvents, silicones, thickeners, softeners, solar filters, antifoaming agents, hydrating agents, perfumes, preservatives, antioxidants, charges, sequestering agents, processing agents, propellants, alkalinizing or acidifying agents, or oily substances.

28. A composition according to any one of Claims 23-27, characterized by the fact that it contains other pigments allowing one to vary the colorings.

29. Application of the composition according to Claim 23 or 26 to the protection of the human epidermis.

30. Application of the composition according to Claim 23 as a makeup product.

31. Application of the composition according to Claim 23 for coloring of human hair.

European  
Patent Office

Application Number  
EP 90 40 0099

### EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT															
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>5</sup> )												
P,X.	EP-A-0 313 380 (ADVANCED POLYMER SYSTEMS, INC.) * Claims; p. 5, lines 53-58; p. 3, line 60 – p. 4, line 1 *	1-3,5, 12-31	A 61 K 7/021 A 61 K 7/13 A 61 K 7/42 A 61 K 7/48 C 08 K 5/341 C 08 L 5/08 C 08 L 33/12 C 08 L 35/04 C 08 L 83/04 C 08 L 89/04												
P,A	GB-A-2 207 153 (L'OREAL ---														
A	FR-A-2 371 917 (F. HOFFMANN-LA ROCHE & CIE, S.A.) ---														
A	GB-A-2 197 885 (L'OREAL) -----														
The present search report has been drawn up for all claims.			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>5</sup> )  A 61 K C 08 K C 08 L												
Place of search THE HAGUE		Date of completion of the search April 24, 1990	Examiner DE LOS ARCOS Y VELAZQUEZ												
<p align="center"><b>CATEGORY OF CITED DOCUMENTS</b></p> <table border="0"> <tr> <td>X: Particularly relevant if taken alone.</td> <td>T: Theory or principle underlying the invention.</td> </tr> <tr> <td>Y: Particularly relevant if combined with another document of the same category.</td> <td>E: Earlier patent document, but published on, or after the filing date.</td> </tr> <tr> <td>A: Technological background.</td> <td>D: Document cited in the application.</td> </tr> <tr> <td>O: Non-written disclosure.</td> <td>L: Document cited for other reasons.</td> </tr> <tr> <td>P: Intermediate document.</td> <td></td> </tr> <tr> <td></td> <td>&amp;: Member of the same patent family, corresponding document.</td> </tr> </table>				X: Particularly relevant if taken alone.	T: Theory or principle underlying the invention.	Y: Particularly relevant if combined with another document of the same category.	E: Earlier patent document, but published on, or after the filing date.	A: Technological background.	D: Document cited in the application.	O: Non-written disclosure.	L: Document cited for other reasons.	P: Intermediate document.			&: Member of the same patent family, corresponding document.
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